Enhancement of the electric dipole moment of the electron in the YbF molecule[*]

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We calculate an effective electric field on the unpaired electron in the YbF molecule. This field determines sensitivity of the molecular experiment to the electric dipole moment of the electron. We use experimental value of the spin-doubling constant γ to estimate the admixture of the configuration with the hole in the 4f-shell of Ytterbium to the ground state of the molecule. This admixture reduces the field by 7%. Our value for the effictive field is 5.1 a.u. $= 2.5 \cdot 10^{10}$ V/cm.

Introduction

It is well known that effects caused by an electric dipole moment (EDM) of the electron d_e are strongly enhanced in heavy diatomic radicals (see, for example, a review [1]). An experimental search for the EDM of the electron is now underway in Brighton University on the YbF molecule [2]. For this reason the reliable calculations for this molecule are necessary. The existence of a shallow 4f-shell adds complexity to such calculations. Here we extend the semiempirical approach suggested in [3,4] to account for a possible admixture of the configuration with the hole in the 4f-shell of Ytterbium. The idea that f-hole can explain small value of the spin-doubling constant γ belongs to I. B. Khriplovich [5].

The EDM experiments with radicals are made on the spin-rotational levels of the electronic ground state. The spin-rotational degrees of freedom of the molecule are described by the following spin-rotational Hamiltonian [6–9]:

$$H_{\mathrm{sr}} = B\mathbf{N}^2 + \gamma \mathbf{S}\mathbf{N} + \mathbf{S}\underline{\underline{\mathbf{A}}}\mathbf{I} + W_d d_e \mathbf{S}\mathbf{n}. \tag{1}$$

In this expression $\mathbf{N}$ is the rotational angular momentum, B is the rotational constant, $\mathbf{S}$ is the spin of the electron and $\mathbf{I}$ is the spin of the Yb nucleus, $\mathbf{n}$ is the unit vector directed along the molecular axis from Yb to F. The spin-doubling constant γ characterizes the spin-rotational interaction. The axial tensor $\underline{\underline{\mathbf{A}}}$ describes magnetic hyperfine structure. It can be determined by two parameters: $A = (A_\parallel + 2A_\perp)/3$ and $A_{\mathrm{d}} = (A_\parallel - A_\perp)/3$. The last term in (1) correspond to the interaction of the EDM of the electron d_e with the molecular field, $\frac{1}{2}W_d$ being the effective electric field on the electron.

Parameters B, γ, A and A_{d} are known from the experiment [10–12]:

$$B = 7237 \text{ MHz}, \quad \gamma = 13 \text{ MHz}, \quad A = 7617 \text{ MHz}, \quad A_{\mathrm{d}} = 102 \text{ MHz}, \tag{2}$$

while W_d have to be calculated. There are three calculations of this parameter [4,13,14]. In earlier calculations [4,13] 4f-shell of Ytterbium was frozen. In [14] f-electrons are included in the valence space, but details of this calculation are not yet published. Here we allow the admixture of the f-hole to the ground state of the molecule.

Electronic wave function

The ground state of YbF molecule is known to be $\Sigma_{1/2}$ [10]. The large hyperfine constants A and A_{d} indicate that unpaired electron occupies molecular orbital σ_{s} with dominant contribution from 6s-orbital and significant contribution of $6p_0$-orbital of Yb ion. But a simple one-configurational wave function can not explain an exceptionally small value of the constant γ. Following Khriplovich we will assume that there is small admixture of the f-hole:

$$|\Sigma, \omega\rangle = |\sigma_{\mathrm{s}}, \omega\rangle + \delta_{\mathrm{f}}\overline{|\sigma_{\mathrm{f}}, -\omega\rangle}, \tag{3}$$

where $\omega = \pm\frac{1}{2}$ is the projection of the total electronic angular momentum on the molecular axis and the bar over the orbital corresponds to the hole. More explicitly (3) means that many electron wave function reads

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[*]To be submitted to J. Phys. B

$$|\Sigma,\omega\rangle = [\ldots]\left(|\sigma_{\rm f},-\tfrac{1}{2}\rangle|\sigma_{\rm f},\tfrac{1}{2}\rangle|\sigma_{\rm s},\omega\rangle + \delta_{\rm f}|\sigma_{\rm f},\omega\rangle|\sigma_{\rm s},-\tfrac{1}{2}\rangle|\sigma_{\rm s},\tfrac{1}{2}\rangle\right),\tag{4}$$

where $[\ldots]$ denotes the closed core. The spin-orbit interaction for the f-hole is large and has the opposite sign. This can explain the small value of γ (see below).

All constants of the Hamiltonian (1) except for the constant B depend only on the electron spin density in the vicinity of the heavy nucleus. For this reason we can expand molecular orbitals in spherical waves with the origin at the Yb nucleus:

$$|\sigma_{\rm s},\omega\rangle = (x_{\rm s}|\tilde{6}s\rangle + x_{\rm p}|\tilde{6}p_0\rangle + x_{\rm d}|\tilde{5}d_0\rangle + \ldots)|\omega\rangle,\tag{5}$$

$$|\sigma_{\rm f},\omega\rangle = (|\tilde{4}f_0\rangle + \varepsilon_{\rm d}|\tilde{5}d_0 + \ldots\rangle)|\omega\rangle,\tag{6}$$

where $|\omega\rangle$ denotes spin function and dots stand for the higher spherical waves. The radial functions in this expansion can be considered as distorted orbitals of the Yb$^+$ ion. Corresponding principle quantum numbers are marked with tilde.

Wave function (3) is written in a pure nonrelativistic coupling case. Spin-orbit interaction $H_{\rm so}$ mixes state (3) with $\Pi_{1/2}$ states. One can expect that the largest admixtures correspond to the molecular orbitals $\pi_{\rm p}$ and $\pi_{\rm f}$ (the spin-orbit interaction for the 5d-shell is much smaller):

$$|\pi_{\rm p},\omega\rangle = (a_{\rm p}|\tilde{6}p_{2\omega}\rangle + \ldots)|-\omega\rangle,\tag{7}$$

$$|\pi_{\rm f},\omega\rangle = (|\tilde{4}f_{2\omega}\rangle + \ldots)|-\omega\rangle.\tag{8}$$

Then, the wave function of the ground state has the form

$$|\Sigma,\omega\rangle = |\sigma_{\rm s},\omega\rangle + c_{\rm p}|\pi_{\rm p},\omega\rangle + \delta_{\rm f}\overline{|\sigma_{\rm f},-\omega\rangle} + c_{\rm f}\overline{|\pi_{\rm f},-\omega\rangle}.\tag{9}$$

Hyperfine tensor and parameter W_d

The operator of the hyperfine interaction in atomic units has the form

$$H_{\rm hf} = \frac{g_{\rm n}\alpha}{2m_{\rm p}}(\vec{\alpha}\times\mathbf{r}\cdot\mathbf{I})\frac{1}{r^3},\tag{10}$$

where $g_{\rm n}$ is the nuclear g-factor, α is the fine structure constant, $m_{\rm p}$ is the proton mass and $\vec{\alpha}$ is the vector of Dirac matrices. This operator is known to be almost diagonal in quantum number l and in the following calculations we neglect nondiagonal terms.

Let us start with the nonrelativistic expressions for a spherical wave $l \neq 0$. It is not difficult to derive, that for the σ-type state $|l,0\rangle$

$$A = 0, \qquad A_{\rm d} = \frac{g_{\rm n}\alpha^2}{2m_{\rm p}}\frac{l(l+1)}{(2l-1)(2l+3)}\langle n,l|\frac{1}{r^3}|n,l\rangle.\tag{11}$$

So, in the nonrelativistic approximation only s-wave contributes to the isotropic constant A. Note that the radial integral in (11) is rapidly decreasing with l, while the coefficient in front of it is a weak function of l.

Interaction of the EDM of the electron with the molecular electric field $-\nabla\phi$ is also singular at the nucleus [15]. The most convenient form of this operator is [16]:

$$H_d = 2d_{\rm e}\begin{pmatrix}0 & 0\\0 & \vec{\sigma}\end{pmatrix}(-\nabla\phi).\tag{12}$$

Relativistic expressions for A, $A_{\rm d}$ and W_d can be found in [3,4,1]. In the paper [4] these constants were calculated for the wave function (9) with $c_{\rm p} = \delta_{\rm f} = c_{\rm f} = 0$:

$$A = \left(11850x_{\rm s}^2 - 102x_{\rm p}^2 - 5x_{\rm d}^2 + \cdots\right)\ {\rm MHz},\tag{13}$$

$$A_{\rm d} = \left(422x_{\rm p}^2 + 36x_{\rm d}^2 + \cdots\right)\ {\rm MHz},\tag{14}$$

$$W_d = (-29.7x_{\rm s}x_{\rm p} + 1.3x_{\rm p}x_{\rm d} + \cdots)\ {\rm a.u.}\tag{15}$$

If we neglect the d-wave terms and use the experimental values (2) for A and A_d, we can solve (13) – (15) for x_s, x_p and W_d:

$$x_s = 0.803, \qquad x_p = 0.492, \tag{16}$$

$$W_d = -11.7 \text{ a.u.} = -1.45 \cdot 10^{25} \text{Hz/(e cm)}, \tag{17}$$

where sings of x_s and x_p are chosen to account for the repulsion of the unpaired electron from the F$^-$ ion.

Result (17) is more accurate than one can expect from (13) – (15). It follows from the proportionality between W_d and $\sqrt{AA_d}$:

$$W_d = -1.69 \cdot 10^{16} \sqrt{AA_d} \ 1/(\text{e cm}), \tag{18}$$

which is based on the behaviour of s- and p-waves in the vicinity of the nucleus where molecular potential is close to that of the nucleus. In contrast to that, results (16) depend on the assumption that spherical waves in (5) correspond to the orbitals of Yb$^+$.

Below we calculate several corrections to (17) and (18), which mostly account for contribution of the higher spherical waves. If we use the normalization condition $x_s^2 + x_p^2 + x_d^2 \approx 1$, we can solve equations (13) – (15) with the d-wave included:

$$x_s = 0.803; \quad x_p = 0.481, \quad x_d = 0.356, \quad W_d = -11.2 \text{ a.u.} \tag{19}$$

Comparison of (17) and (19) gives the following correction coefficient for the d-wave contribution to W_d:

$$k_d = 0.96. \tag{20}$$

Note that the normalization condition give the upper bound for the coefficient x_d. So, it is likely, that (19) and (20) somewhat overestimate the d-wave contribution.

Spin-doubling constant

Let us estimate the mixing coefficient c_p in (9):

$$c_p = \frac{\langle \Pi(A_1)|H_{so}|\Sigma(X)\rangle}{E_X - E_A} = \frac{\langle \pi_p, \omega|H_{so}|\sigma_s, \omega\rangle}{E_X - E_A} \approx \frac{x_p a_p \xi_{6,1}}{\sqrt{2}(E_X - E_A)}, \tag{21}$$

where we use (5) and (7) to calculate the numerator:

$$\langle \pi_p, \omega|H_{so}|\sigma_s, \omega\rangle \approx x_p a_p \langle \tilde{6}p_1, -\tfrac{1}{2}|H_{so}|\tilde{6}p_0, \tfrac{1}{2}\rangle \approx x_p a_p \langle 6p_1, -\tfrac{1}{2}|H_{so}|6p_0, \tfrac{1}{2}\rangle, \tag{22}$$

$$\langle n, l, 1, -\tfrac{1}{2}|H_{so}|n, l, 0, \tfrac{1}{2}\rangle \equiv -\xi_{n,l}\langle l, 1|l_1|l, 0\rangle\langle -\tfrac{1}{2}|s_{-1}|\tfrac{1}{2}\rangle = \tfrac{1}{2}\xi_{n,l}\sqrt{l(l+1)}, \tag{23}$$

and $\xi_{n,l}$ is the atomic spin-orbit constant for the (n, l)-shell. It is proportional to the radial integral which enters (11). For the Yb$^+$ ion $\xi_{6,1} = 1900$ cm^{-1}.

The level (7) is identified as A$_1$ (E_{A_1}=18090 cm^{-1}). It's fine splitting with the level A$_2$ ($\Pi_{3/2}$) is 1370 cm^{-1} [10]. Within the same approximation we can link this splitting to the constant $\xi_{6,1}$ and find parameter a_p:

$$E_{A_2} - E_{A_1} \approx a_p^2 \xi_{6,1}, \quad \Rightarrow \quad a_p^2 \approx 0.72. \tag{24}$$

In a same manner we can calculate coefficient c_f in (9). In this case the spin-orbit interaction mixes σ_f-hole with π_f-hole:

$$c_f = \frac{\langle \Pi(F)|H_{so}|\Sigma(X)\rangle}{E_X - E_F} \approx \delta_f \frac{\overline{\langle \pi_f, -\omega|H_{so}|\sigma_f, -\omega\rangle}}{E_X - E_F} \approx \frac{-\sqrt{3}\delta_f \overline{\xi}_{4,3}}{E_X - E_F}. \tag{25}$$

The only problem here is that molecular state with the π_f-hole, which we define as $\Pi(F)$, is not known, and thus we do not know the energy denominator. The spin-orbit constant for the f-hole has the opposite to normal sign: $\overline{\xi}_{4,3} = -3665$ cm^{-1}.

Formulae (21), (24) and (25) reduce the number of independent parameters in the wave function (9). Still, it has two extra parameters δ_f and ε_d as compared to the wave function (5) which was used in (13) – (15). Below we eliminate parameter δ_f using experimental value of the spin-doubling constant γ.

The spin-doubling term in the effective Hamiltonian (1) arise from the spin-orbit interaction. It was shown in [9] that

$$\gamma = 2B \left(1 - \langle \Sigma(X), \tfrac{1}{2} | J_{e,+} | \Sigma(X), -\tfrac{1}{2} \rangle \right),$$ (26)

where $\mathbf{J}_e = \mathbf{L} + \mathbf{S}$ is the total angular momentum of the electrons. For the pure Σ state $\langle \mathbf{J}_e \rangle = \langle \mathbf{S} \rangle$ and (26) gives $\gamma = 0$. This is no longer true, when the spin-orbit corrections are taken into account. With the help of (26), (21) and (25) it is easy to calculate γ for the state (9):

$$\gamma = 2B \left(2(x_{\mathrm{p}} a_{\mathrm{p}})^2 \frac{\xi_{6,1}}{E_X - E_A} + 12\delta_{\mathrm{f}}^2 \frac{\overline{\xi}_{4,3}}{E_X - E_F} \right).$$ (27)

Note that numerical factors in parentheses are equal to $l(l+1)$.

As we already pointed out, the second denominator in (27) is unknown. If we use corresponding energy interval for the Yb$^+$ ion, we receive the following relation between x_{p} and δ_{f}

$$2100x_{\mathrm{p}}^2 - 11150\delta_{\mathrm{f}}^2 = 13, \quad \Rightarrow \quad \delta_{\mathrm{f}}^2 \approx 0.19x_{\mathrm{p}}^2.$$ (28)

This equation shows that experimental value of γ correspond to almost complete cancelation between p-wave and f-wave contributions. To obtain this relation between δ_{f} and x_{p} we used ionic spin-orbit constants $\xi_{n,l}$ and ionic denominator in (27). So, we can not expect it to be much better than an order of magnitude estimate.

Spin-orbit and f-hole corrections to W_d

It follows from (11), (27) and (28), that for the molecular state (9) the f-wave contribution to the constant A_{d} should be approximately 6 times smaller than that of the p-wave. Indeed, the two contributions to the constant γ cancel each other, but in (27) there is the factor $l(l+1)$ which is not present in (11).

A straightforward relativistic calculation result in the following f-hole correction to the hyperfine tensor

$$\delta A = -\frac{g_{\mathrm{n}} \alpha}{2m_{\mathrm{p}}} \delta_{\mathrm{f}}^2 \left(\frac{12}{49} h_{5/2,5/2} + \frac{32}{49} h_{5/2,7/2} + \frac{64}{147} h_{7/2,7/2} \right) \text{ a.u.},$$ (29)

$$\delta A_{\mathrm{d}} = \frac{g_{\mathrm{n}} \alpha}{2m_{\mathrm{p}}} \delta_{\mathrm{f}}^2 \left(\frac{48}{245} h_{5/2,5/2} - \frac{8}{49} h_{5/2,7/2} + \frac{64}{441} h_{7/2,7/2} \right) \text{ a.u.}$$ (30)

The radial integrals $h_{j,j'}$ here have the form $h_{j,j'} = \int_0^\infty \mathrm{d}r \, (f_j g_{j'} + g_j f_{j'})$, where f_j and g_j are the upper and lower components of the radial Dirac wave function. Again we take radial integrals for the Yb$^+$ ion and use (28) to arrive at

$$\delta A = -11x_{\mathrm{p}}^2 \text{ MHz}, \qquad \delta A_{\mathrm{d}} = 64x_{\mathrm{p}}^2 \text{ MHz}.$$ (31)

It is clear, that correction (31) to isotropic constant A (13) is negligible, while correction to the dipole constant A_{d} (14) is about 15% for a given x_{p}, which is in a good agreement with our nonrelativistic estimate $\frac{1}{6}$.

With the f-hole correction (31) included, equation (14) is changed to

$$A_{\mathrm{d}} = \left(486x_{\mathrm{p}}^2 + 36x_{\mathrm{d}}^2 \right) \text{ MHz},$$ (32)

and we obtain the following f-hole correction coefficient to W_d

$$k_{\mathrm{f}} = 0.93.$$ (33)

In deriving (33) we have ignored the direct f-wave contribution to the constant W_d (see (15)). Such contribution is proportional to a small product $x_{\mathrm{d}}\delta_{\mathrm{f}} \leq 0.1$ and is less than 1%.

The last correction to the constant W_d is associated with the admixture of the π_{p} state to (9). According to (21) $c_{\mathrm{p}} \approx -0.06x_{\mathrm{p}}$. This admixture changes weights of the p$_{1/2}$- and p$_{3/2}$-waves in the wave function. That, in turn, slightly changes coefficients in (14) and (15) (note, that only p$_{1/2}$-wave contributes to W_d). A simple calculation give

$$k_{\mathrm{so}} = 0.98.$$ (34)

Discussion

Taking into account (20), (33) and (34), we obtain the total correction factor for W_d to be $k_{\text{corr}} = k_{\text{d}} k_{\text{f}} k_{\text{so}} = 0.87$. Applying it to (18), we arrive at

$$W_d = -10.2 \text{ a.u.} = -1.26 \cdot 10^{25} \text{Hz/(e cm)}. \tag{35}$$

We have calculated corrections to the semiempirical value of the constant W_d of the spin-rotational Hamiltonian (1) which can account for the P,T-odd effects in YbF molecule. The main correction is caused by the f-hole admixture to the ground state. Two other corrections account for the spin-orbit interaction and for the d-wave term in the wave function. Altogether they reduce the answer by more than 10%.

We think that wave function (9) includes two most important configurations. Admixture of other configurations will tend to decrease constant W_d, so we can expect that our value (35) is slightly overestimated. But it is unlikely, that corresponding corrections are significantly larger than those discussed above. So, we estimate the accuracy of our calculation to be about 20%, which is typical to the semiempirical method.

Ab initio calculation [13] gave smaller absolute value for W_d, but it also underestimated both A and A_{d}. It is more informative to compare the coefficient in the equation (18) which correspond to different calculations. Our final value for this coefficient is $-1.47 \cdot 10^{16}$ 1/(e cm), while results of [13] correspond to $-1.75 \cdot 10^{16}$ 1/(e cm). So, in this sense, our result is even smaller than that of [13].

In this paper we have not considered other possible sources of P,T-violation, such as scalar neutral currents [7] and magnetic quadrupole moment of the nucleus [17]. Corresponding constants W_S and W_M of the spin-rotational Hamiltonian can be calculated in a similar way to W_d [4]. Our value for the former constant is: $W_S = -43$ kHz. Because of the higher multipolarity of the electronic operator associated with the constant W_M, this interaction is much more sensitive to the higher terms of the spherical wave expansion of the molecular wave function. Thus, it is more difficult to make accurate calculation of this interaction within the semiempirical approach.

Acknowledgments

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